

Silica Scale Management: Lowering Operating Costs through Improved Scale Control, and Adding Value by Extracting Marketable By-Products

E. A. Burton, W. L. Bourcier, A. Wallace, C. J. Bruton, R. Leif

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

This article was submitted to
Geothermal Resources Council 2003 Annual Meeting, Morelia,
Michoacan, Menico, October 12, 15, 2003

June 18, 2003

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

Silica Scale Management: Lowering Operating Costs through Improved Scale Control, and Adding Value by Extracting Marketable By-Products

Elizabeth A. Burton, William L. Bourcier, Adam Wallace, Carol J. Bruton and Roald Leif
Lawrence Livermore National Laboratory

Key Words: silica, scale, silica extraction, pH-modification, Mammoth

Abstract

We are using laboratory and field experiments to design modeling tools and technology that will improve silica scale management practices in geothermal plants. Our work will help to lower operating costs through improved scale prediction and add new revenue streams from sale of mineral byproducts extracted from geothermal fluids.

Improving the economics and effectiveness of scale control programs and/or extraction systems in geothermal operations requires a coupled kinetic-thermodynamic model of silica behavior. Silica scale precipitation is a multi-step process, involving a nucleation-related induction period, aqueous polymerization, condensation of polymers to form colloids, and deposition onto a solid surface. Many chemical and physical variables influence the rates of these steps and their impacts must be quantified and predictable in order to optimally control silica behavior. To date, in laboratory studies, we have quantified the effects on silica polymerization of the following set of chemical variables: Na at 500 and 2000 ppm, pH values from 5 to 9, temperatures of 25 and 50°C, and silica saturation values from 1.2 to 6 at initial dissolved silica concentrations of 600 ppm. Lowering pH both increases the induction time prior to polymerization and decreases the polymerization rate. We have successfully used a multiple regression model to predict polymerization rates from these variables.

Geothermal fluids contain significant dissolved concentrations of potentially valuable mineral resources such as zinc, lithium, cesium and rubidium, but silica fouling interferes with traditional extraction methods. We are developing customized and new technologies to extract the silica as a commercial-grade commodity as well as the valuable metals. We are conducting field testing of some of these techniques at a Mammoth, CA geothermal plant using a reverse osmosis unit to concentrate the fluid, adding a commercial agglomerating agent to promote silica precipitation, and then removing the silica using a tangential flow ultrafilter. The particle size, surface area and trace impurities of the silica are characterized for comparison with commercial-grade silica products. We are also testing ion exchange resins and other functionalized materials to extract potentially economic concentrations of lithium, cesium, and rubidium that are enriched in the reverse osmosis concentrate.

Introduction

Silica scaling is a common problem in geothermal facilities. Geothermal operators need improved tools to evaluate and mitigate the impact of silica scaling. It is also proving feasible to develop technologies to economically convert silica and other dissolved elements in geothermal fluids from a problem to a resource. The benefits to a geothermal operation of controlling silica in geothermal fluids include:

- a. Lower operating and maintenance costs, including mitigation costs associated with silica scaling;
- b. Improved heat transfer performance;
- c. Decreased costs and minimized environmental impact associated with chemical additives;
- d. The addition of new revenue streams from mineral extraction, when appropriate.

To achieve these benefits, we are developing a predictive model of silica deposition and the technologies to economically remove silica with appropriate properties for sale in industrial markets. The removal of silica also is a necessary precursor to extracting other valuable dissolved elements from geothermal fluids owing to its fouling of extraction equipment. Our studies include both laboratory testing and field trials. When deployed, the results will allow plant operators and technical staff to:

- a. Predict silica scaling rates and magnitudes for conditions covering the range of water chemistries found in geothermal plants and potential resources;
- b. Determine treatment type and minimum dosage of chemical agents (pH modification or various types of inhibitors) to control scaling;
- c. Evaluate the potential for creating new revenue from silica and other elements and to identify the appropriate technologies for their extraction.

Background

Predictive modeling of scale deposition: Effective prediction of silica scaling and design of scale control programs and/or extraction systems in geothermal operations requires a coupled kinetic-thermodynamic model of silica behavior. Silica scale precipitation is a time-dependent, multi-step process, involving aqueous polymerization, condensation of polymers to form colloids, and deposition onto a solid surface (e.g., Iler, 1979; Weres et al., 1980; Weres et al., 1981). While thermodynamic models exist that predict the potential magnitude of scaling and qualitatively capture the overall dependence of reaction rates on the degree of disequilibrium, they do not capture the overall and step-specific rate effects of various other solution parameters, including sodium and fluoride concentrations, and pH.

Scale control programs involve the use of chemical inhibitors that retard or disrupt specific steps and/or change fluid chemistry to retard overall rates such that the fluid moves beyond scale-sensitive plant facilities before scale precipitates. Optimizing silica extraction techniques and economics depends critically on understanding how to change conditions to control rates of reaction and the physical and chemical properties of precipitates. Consequently, understanding and incorporating the kinetics of precipitation is critical to efficient and cost-effective management of silica scaling.

Extraction of marketable silica and minerals: Geothermal fluids contain significant dissolved concentrations of potentially valuable mineral resources such as silica, zinc, lithium and cesium (Gallup, 1998). This mineral content has often been considered more of a nuisance than an asset, but interest is increasing in co-producing and marketing some of these constituents. However, the geothermal industry lacks simple, cost-effective methods to extract mineral by-products from geothermal fluids. We are examining the potential for adaptation of

existing methods from the hydrometallurgical industry, as well as the use of new technologies, such as metal-specific membranes.

To allow high-value fluid components to be removed, the ubiquitous dissolved silica in geothermal fluids first must be removed or reduced in concentration. Most geothermal fluids contain dissolved silica concentrations in equilibrium with quartz at reservoir temperature. In general, the hotter the reservoir is, the higher its dissolved silica concentration. By purposefully precipitating silica as a high surface area, porous material with properties similar to those of commercially precipitated silica, the silica-scaling problem is solved, and at the same time a marketable silica by-product is produced. Other benefits may also be realized, such as additional energy extraction that would not otherwise be economic due to scaling. At the Mammoth, CA binary power plant, silica scaling becomes a problem when the spent geothermal fluid is used in an evaporator to cool the working fluid. Recent field tests (discussed below) show that extracting silica from the Mammoth fluids should minimize scale formation on the evaporative cooling panels (Fig. 1a). The use of processed geothermal fluid would eliminate the need to purchase tertiary water for cooling and thus lower operating costs.

Results and Interpretation

Predictive modeling of scale deposition: Using laboratory tests, we have quantified the effects on silica polymerization of the following set of chemical variables: Na at 500 and 2000 ppm, pH values from 5 to 9, temperatures of 25 and 50°C, and silica saturation values from 1.2 to 6. Total initial dissolved silica concentrations were kept constant at 600 ppm. Silica was added as sodium metasilicate, and pH was adjusted by addition of hydrochloric acid or sodium hydroxide. The final total dissolved solids (TDS) contents of the solutions were 1300 and 5200 ppm. Experimental solutions were held at run temperature $\pm 0.5^\circ\text{C}$ by a circulating water bath. The pH was monitored throughout each run. Silica polymerization was followed over time by withdrawing aliquots of the solution for spectrophotometric measurement using the silicomolybdate method as modified by Iler (1979).

Polymerization rates increase with increasing Na concentration, pH and temperature (Fig. 2), and decrease with decreasing silica concentration. These variables also affect the degree to which the polymerization rate varies with the silica concentration variable (slopes in Fig. 2c and d). The silica concentration variable reflects the control of saturation state on rate. The term for the rate dependence on saturation state has been expressed in a variety of forms (e.g., Goto, 1956, for silica polymerization; Lasaga, 1981, for mineral precipitation/dissolution). We plotted silica concentration as $\log Q$ (where Q is saturation state expressed as the ratio of dissolved silica concentration, C , to the equilibrium concentration with respect to amorphous silica at run temperature, S); as $\log (C-S)$; and as $\log (1-Q)$. We achieved the best fit with the $\log (C-S)$ term (Fig. 2c and d).

Lowering pH both increases the induction time prior to polymerization and decreases the polymerization rate (e.g. Fig. 2a). These results explain field experience where silica scaling has been effectively prevented by pH-modification (e.g., Rothbaum et al., 1979; Gill, 1993). However, our results show that the magnitude of the pH effect depends on the other chemical variables as well. Future experiments will expand the matrix of tests to include the range of

chemistries typical of geothermal plant waters. Longer-term experiments are planned to provide baseline data for modeling the subsequent condensation and deposition steps.

We used multiple linear regression to model rates of polymerization as a function of the above chemical variables and elapsed time. Each chemical variable was input as a predictor variable in log concentration units. This simple model appears to be a good predictor of polymerization rates for the intermediate range of rate measurements (Fig. 3), but is less reliable for rates measured early or near the end of each run. The poorer fit is partly an effect of the induction period and of the detection limits of the molybdate method. Future modeling will quantify the impact of fluid chemical variables on the length of the induction period before polymerization begins, and will also incorporate the kinetics of the condensation and deposition steps.

Extraction of marketable silica and minerals at Mammoth: The relatively low dissolved silica content of 250 ppm in Mammoth fluids presents a challenge to silica extraction. Most geothermal fluids from flash plants contain ≥ 500 ppm. Conventional methods for extracting silica are not effective for the Mammoth fluids because of slow polymerization rates at low silica concentrations. For this reason, we processed the Mammoth geothermal fluid through a reverse osmosis (RO) membrane (Fig. 1b). The RO unit provides a silica-enriched concentrate for silica and other metals removal, and a low TDS permeate for use in the evaporative cooler. The reverse osmosis unit can concentrate the fluid to any desired silica concentration. The optimum silica concentration allows rapid extraction, but does not foul the reverse osmosis membranes with precipitated silica. Silica concentrations between 600 and 700 ppm appeared to satisfy both constraints in our Mammoth field trials.

We used a commercial agglomerating agent to promote silica precipitation and removed the silica using a tangential flow filter. The silica was characterized using a particle size analyzer and a gas adsorption (BET) surface area analyzer, and then digested for chemical analysis. The most promising samples also were sent to commercial laboratories for product testing. We are comparing these test results with the properties of commercial-grade silica products to guide further work in optimizing extracted silica properties for specific markets.

The gas adsorption (BET) surface area of silica precipitates obtained to date are in the range of 40 to 130 m²/g for samples that were air dried at 50°C. These values are near the low end of the range of surface areas of commercial silica, but should increase as our processing and post-processing conditions are optimized. The chemical composition of a representative silica precipitate is given in Table 1. Our Mammoth geothermal silicas are of very high purity, greater than 98 wt % for untreated silica, and about 99.6 wt % for acid rinsed. These compositions compare favorably with commercial precipitated silica that often have 1-5 wt% impurities. The precipitate does contain measurable arsenic. However, the arsenic is less enriched in the silica precipitate than in bulk fluid. The Si/As ratio of the fluid is about 800 vs. 70 in the silica precipitate. A simple acid rinse reduced the arsenic content by about 2/3. Better arsenic removal methods are available and will be investigated.

Of additional interest at Mammoth are the potentially economic concentrations of lithium, cesium, and rubidium that are enriched in the reverse osmosis concentrate. Work is

underway to extract these elements using commercial ion exchange resins, and functionalized carbon/silica aerogels.

Acknowledgments

Funding for these projects has been supplied by the Department of Energy, Office of Geothermal and Wind Technologies, the California Energy Commission, and the Lawrence Livermore National Laboratory program for Laboratory Directed Research and Development. Industrial collaborators include ChevronTexaco and Mammoth Pacific LP. We also appreciate advice and suggestions from Paul Hirtz of Thermochem and Jack Harrar.

References

- Gallup, D.L., 1998. "Geochemistry of geothermal fluids and well scales, and potential for mineral recovery." *Ore Geology Reviews*, v.12, p. 225-236.
- Gill, J.S., 1993. "Inhibition of silica-silicate deposits in industrial waters." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, v. 74, p. 101-106.
- Goto, K., 1956. "Effect of pH on Polymerization of Silicic Acid." *Journal of Physical Chemistry*, v. 60, p. 1007-1008.
- Iler, R.K., 1979. *The Chemistry of Silica*. J. Wiley and Sons, New York, 866 p.
- Lasaga, A.C., 1981. "Rate Laws of Chemical Reactions." In Lasaga, A.C. and R.J. Kirkpatrick, eds., *Kinetics of Geochemical Processes. Reviews in Mineralogy*, v. 8, p. 1-68.
- Rothbaum, H.P., B.H. Anderton, R.F. Harrison, A.G. Rohde, and A. Slatter, 1979, "Effect of Silica Polymerization and pH on Geothermal Scaling." *Geothermics*, v. 8, p. 1-20.
- Weres, O., A. Yee, and L. Tsao, 1980. *Kinetics of Silica Polymerization*. National Technical Information Service, Dept. of Energy LBL7033, 256 p.
- Weres, O., A. Yee, and L. Tsao, 1981. "Kinetics of Silica Polymerization." *Journal of Colloid and Interface Science* v. 84, #2, p. 379-402.

Table and Figure Captions

Table 1. Composition of silica precipitate from Mammoth geothermal fluid for untreated, water-rinsed, and dilute HCl-rinsed silica powders.

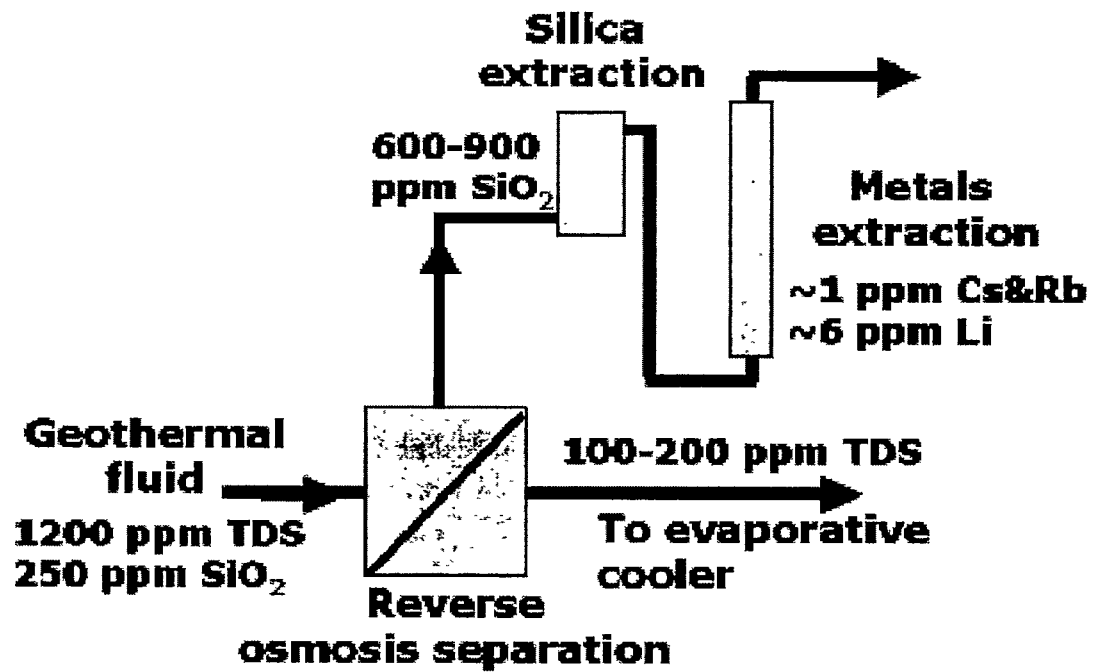
Figure 1. Schematics of Mammoth site: a) binary power plant in which the geothermal fluid is used to heat the isobutane “working fluid” that turns the turbine; b) geothermal fluid processing unit used for silica and metals extraction testing.

Figure 2: Polymerization of silica in test solutions of 600 ppm initial silica at 25°C (a and c) and 50°C (b and d), at pH values from about 5 to 9, and Na concentrations of 500 or 2000 ppm. Legend entries show pH and Na concentrations. Upper diagrams show measured values of molybdate active silica (in ppm) over time; bottom diagrams show the same data expressed as polymerization rate (change in molybdate active silica concentration per change in time, in ppm/hr) vs $\log(C-S)$ where C is concentration in solution and S is the concentration of silica in ppm at equilibrium with amorphous silica at run temperature.

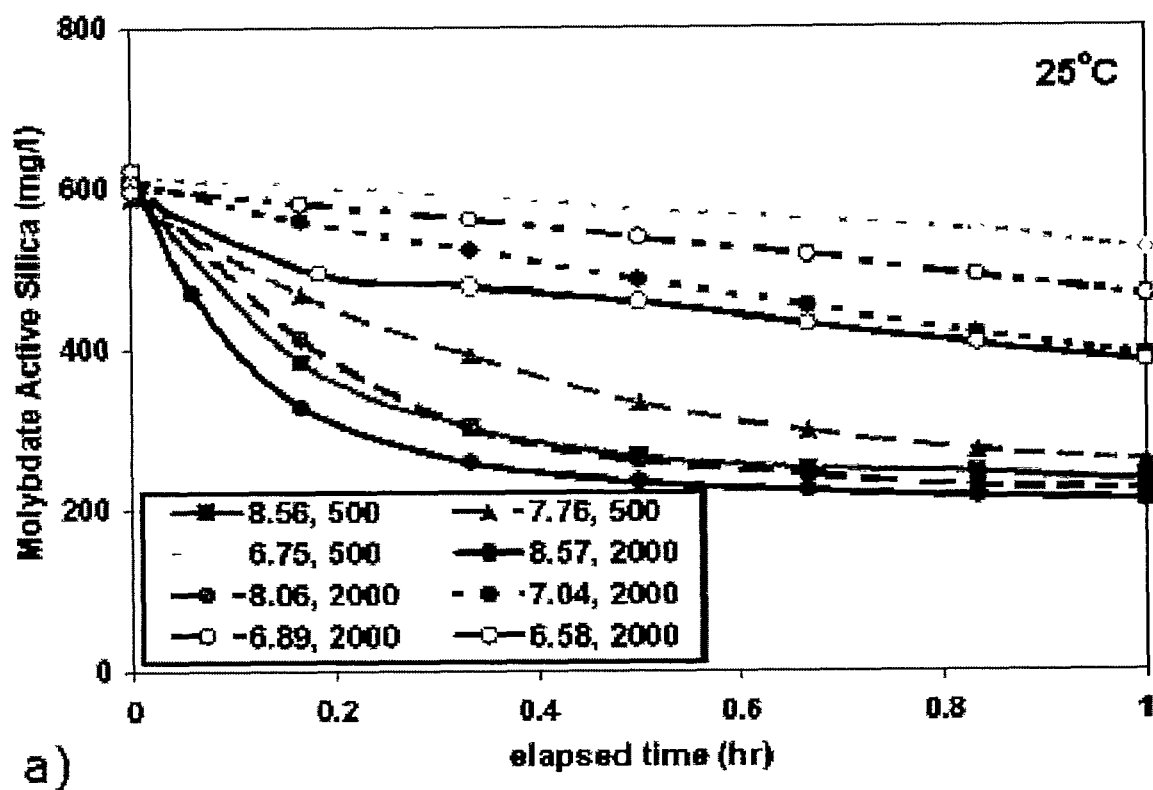
Figure 3: Results of multiple linear regression model for silica polymerization predicted from Na concentration, pH, temperature, elapsed time, and degree of disequilibrium for amorphous silica, expressed as $\log(C-S)$.

	Untreated	DI Rinse	Acid Rinse
Major components in wt %			
SiO₂	98.09	99.13	99.63
Al₂O₃	0.33	0.31	0.31
Fe₂O₃	0.22	0.22	0.20
NhO	0.01	0.01	0.01
MgO	0.13	0.12	0.04
CaO	0.17	0.15	0.02
Na₂O	1.15	0.08	0.02
K₂O	0.15	0.05	0.00
TiO₂	0.01	0.00	0.00
P₂O₅	0.03	0.03	0.02
Total	100.28	100.11	100.26
Minor components in ppm			
As	450	304	162
Au	0.07	0.06	0.05
Cs	21	18	5
Hg	4	4	1
Mo	20	18	10
Sb	350	332	200
Sc	0.3	0.3	0.2
W	31	26	15
Cu	14	13	10
Zn	126	175	46

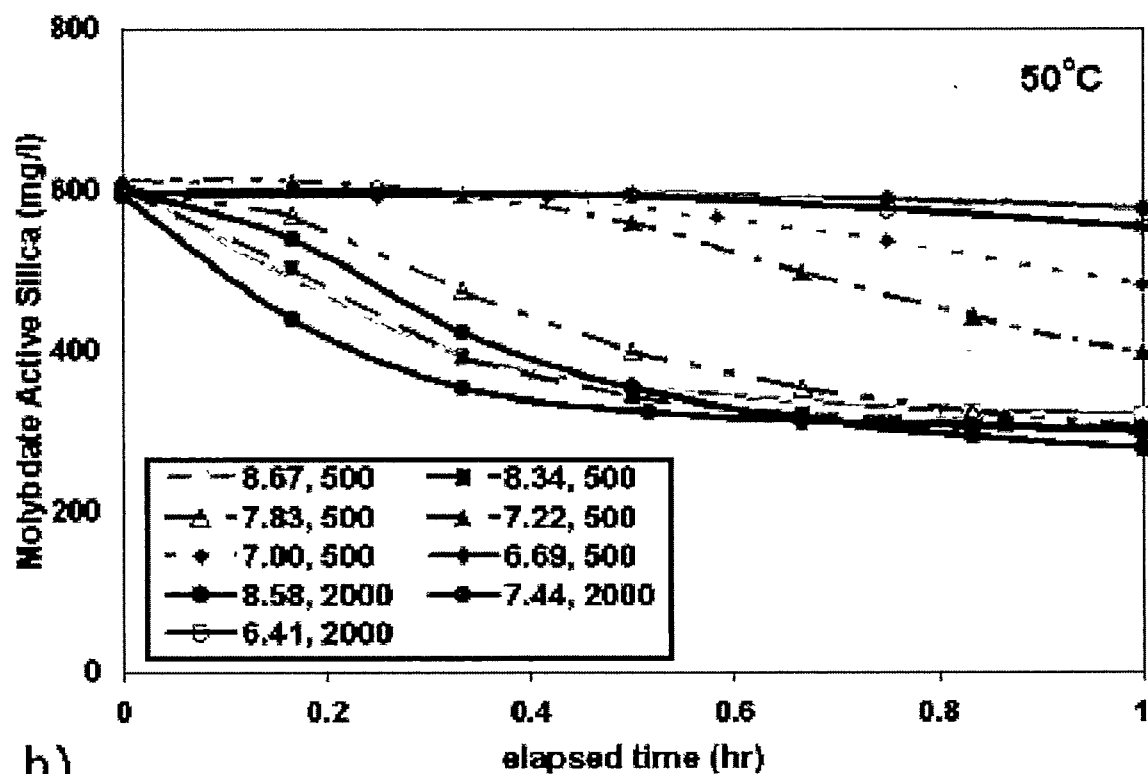
GRC2003 Burton Table 1.TIF



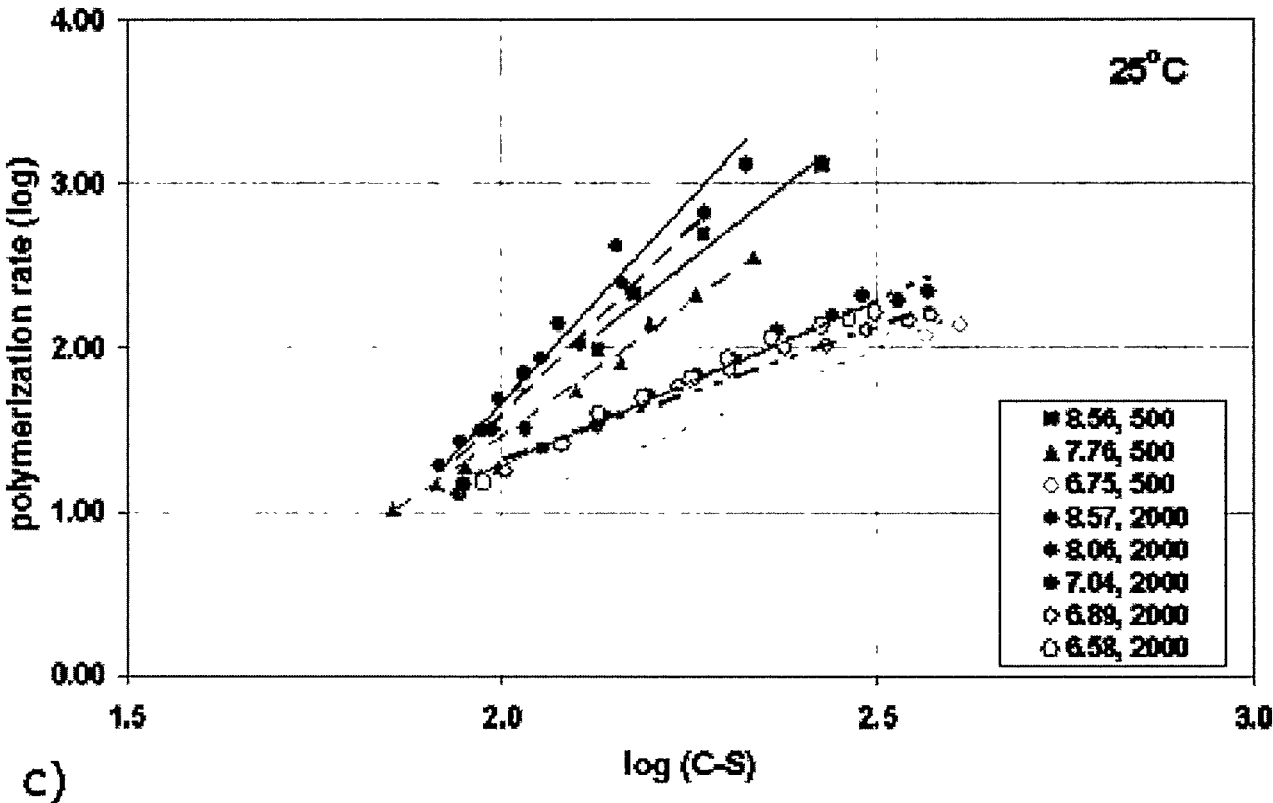
b)



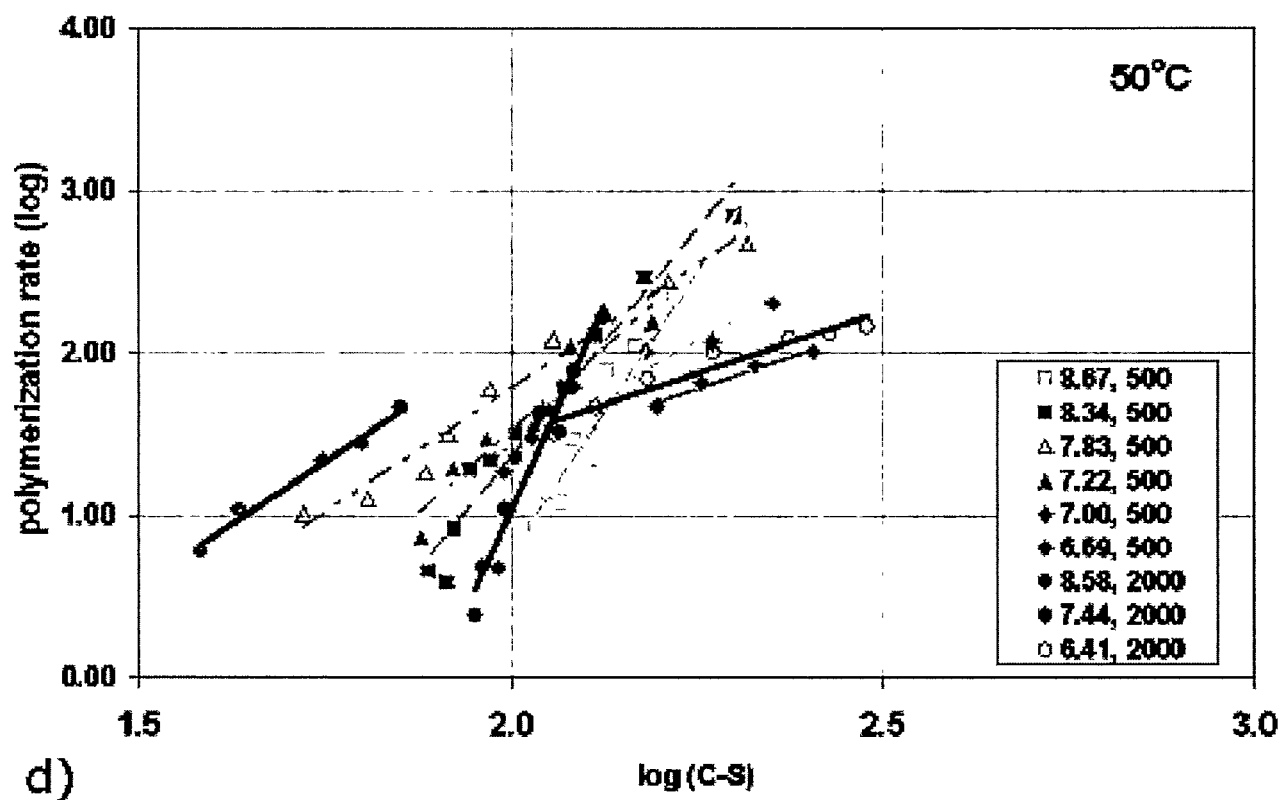
GRC2003 Burton Fig 2A.TIF



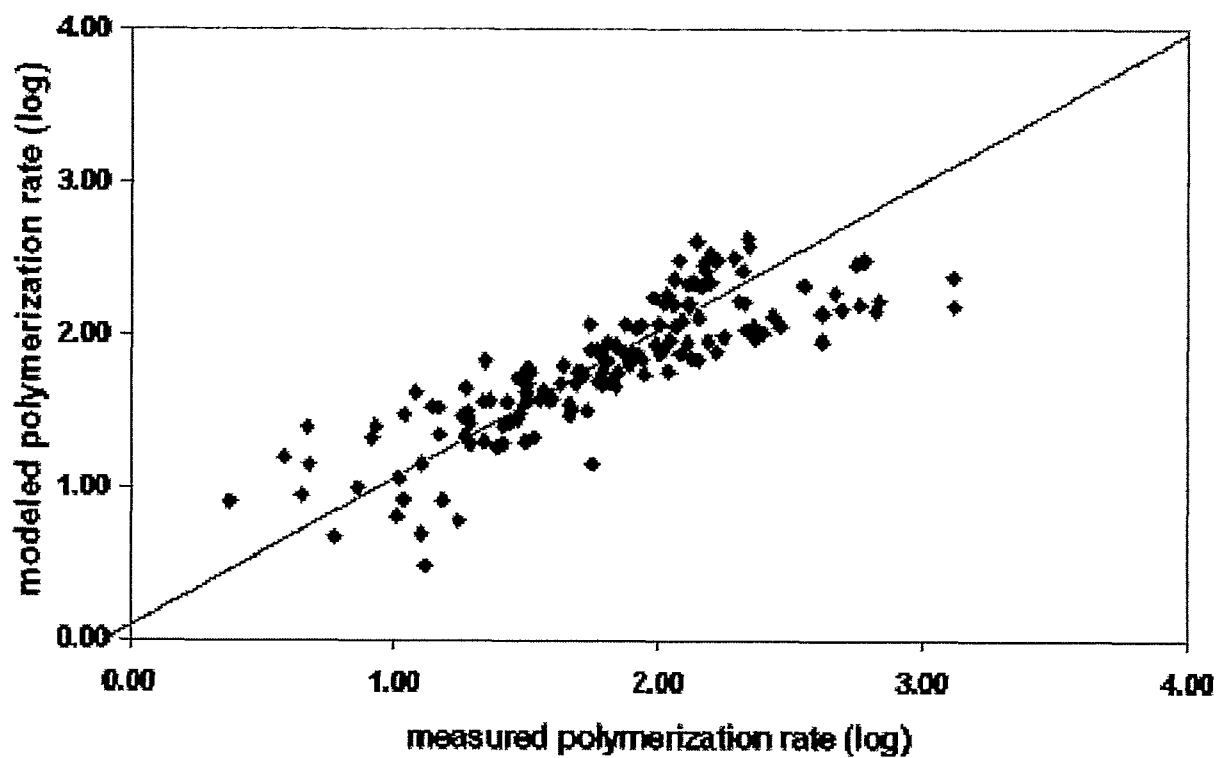
GRC2003 Burton Fig 2B.TIF



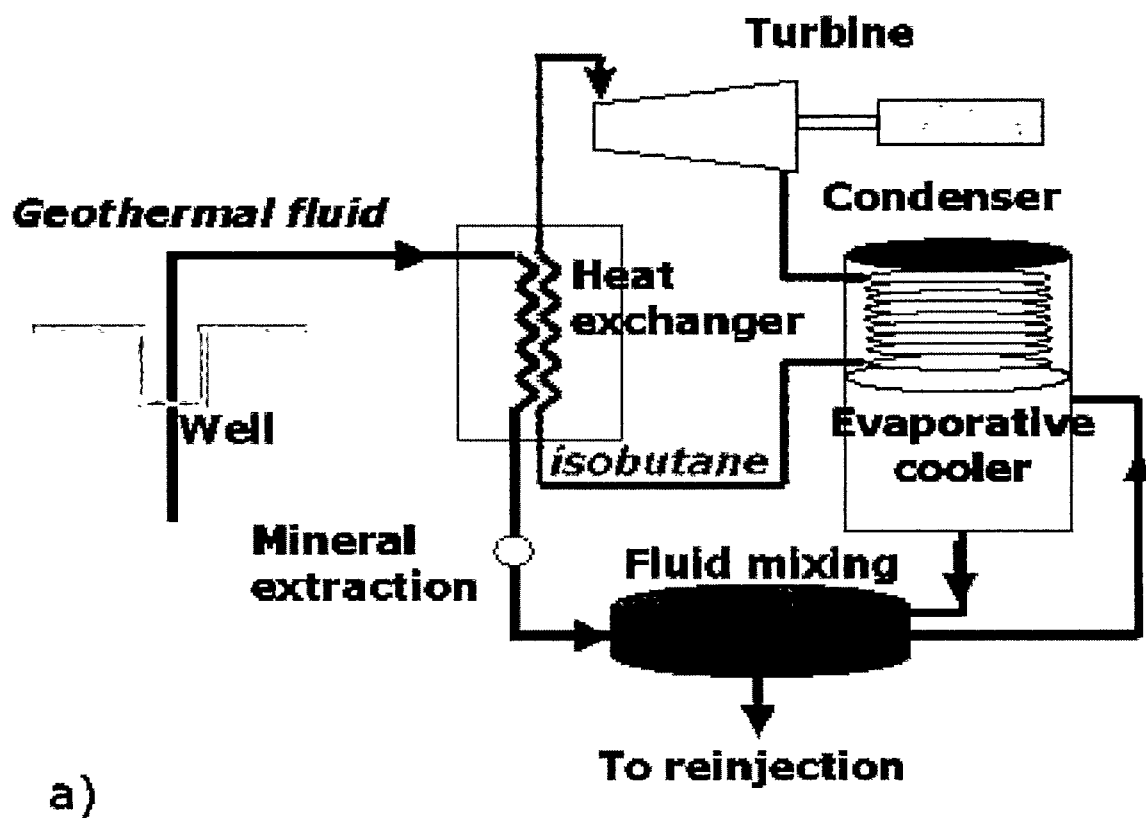
GRC2003 Burton Fig 2C.TIF



GRC2003.Burton Fig 2D.TIF



GRC2003 Burton Fig 3.TIF



GRC2003:Burton Fig 1A.TIF

Burton.LLNL.doc